Sorption of Inorganic and Total Phosphorus from Dairy and Swine Slurries to Soil

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ABSTRACT

Understanding P sorption from animal manures is essential to formulate best management practices with regard to land application of manure from the standpoint of crop production and environmental quality. Little research has focused on the construction of P sorption isotherms where the P source is manure. The objectives of this study were to: (i) develop a procedure to characterize how inorganic P (P_i) and total P (P_t) from dairy slurry and swine slurry sorbs to soil; and (ii) compare the sorption characteristics of P_i and P_t where the P source was dairy slurry, swine slurry, or potassium phosphate (KH_2PO_4). Sorption solutions were prepared in 0.1 M KCl at pH 6 and equilibrated with soils at a 1:25 (w/v) soil/solution ratio for 24 h. Inorganic P, P_t, Al, and Fe in the equilibrated solutions were measured. For all soils, P_i and P_t sorption capacity of dairy slurry was greater than KH_2PO_4. Total P sorption capacity of swine slurry was greater than KH_2PO_4, while P_i sorption capacity was less than KH_2PO_4. Overall, P_i and P_t sorption strengths of the manure slurries were less than or equal to KH_2PO_4. Increased P_i sorption from dairy slurry was correlated with Fe and Al desorption. Reduction of P_i sorption capacity from swine slurry was related to preferential sorption of organic P. Additional studies need to be conducted to determine how differences in P sorption between manures and fertilizer impact in-field P availability to a crop and potential for losses in runoff water.

I N 2000, the USEPA reported that agriculture was the leading source of surface water pollution, affecting 18% of the assessed rivers, streams, and lakes (USEPA, 2002). Agriculture contributed to approximately 45% of the reported water quality problems in impaired rivers, streams, and lakes. This is less than the 1994 estimate that agriculture contributed to 70% of the impairment in the water quality of rivers and lakes (USEPA, 1994). However, further reducing pollution from agriculture is required to improve the quality of our waters.

Studies have shown that excessive application of P in the form of animal manure and/or inorganic fertilizer is responsible for the accumulation of soil P to levels in excess of crop requirements (Sharpley et al., 1984; Sims, 1993). Such soils present a risk to water quality if the P is transported to surface water and accelerates eutrophication. Eutrophication has the potential to impair water quality by restricting a water body's use for fisheries, recreation, industry, and drinking purposes (Sharpley and Menzel, 1987; Sharpley et al., 1998). Phosphorus is strongly adsorbed by most soils; thus, loss of P through eroded sediments during surface runoff is generally of greater concern than leaching (Sharpley et al., 1998). Phosphorus sorption characteristics, such as sorption capacity and sorption strength, of a given soil likely affect the potential for P losses to surface waters both as soluble and particulate P. To reduce the environmental impact of P from agricultural soils, it is important to understand the mechanisms of P sorption to soil colloid surfaces.

The focus of recent P sorption research has been to construct P sorption isotherms, using solutions of KH_2PO_4, to determine if soil P sorption characteristics change after application of manure or fertilizer compared to untreated soils. In general, soil P sorption capacity and strength have been found to change with the application of manure or fertilizer, with reductions in both properties more common than increases (Mozaffari and Sims, 1994; Sharpley, 1996; Holford et al., 1997; Siddique and Robinson, 2003; Laboski and Lamb, 2004). In a Minnesota study, Laboski and Lamb (2004) found that manure application increased, reduced, or did not change sorption capacities of seven soils. They also reported that soils with a manure history had reduced or unchanged sorption strength when compared to the same soils without a manure application history. In another study, P sorption capacity and strength were reduced when soils were treated with manures from various animal species, sewage effluent, or superphosphate (Holford et al., 1997). The magnitude of the decrease in sorption capacity and strength depended on the amount of manure or effluent applied over time; with increased application rates causing a greater reduction in the sorption capacity and strength (Holford et al., 1997).

The observed decreases in P sorption capacity have been suggested by several researchers to be caused by anions of organic acids competing for P sorption sites (Swenson et al., 1949; Nagarajah et al., 1970; Kafkafi et al., 1998). When organic amendments are added to soils, organic acids may be added as part of this amendment directly and/or as a result of microbial decomposition of the amendment. Reduction of P sorption can be caused by the preferential blocking of retention sites or by displacement of sorbed P by anions of these organic acids (Swenson et al., 1949; Kafkafi et al., 1998). Bolan et al. (1994) and Nagarajah et al. (1970) found that P sorption decreased with addition of organic acids and the decrease was dependent on the stability of the complexes formed with Al and Fe. Inositol hexaphosphate (IHP), a form of organic P in animal manures, was found to preferentially sorb to soil compared to inorganic P (Anderson et al., 1974). Inositol hexaphosphate also released orthophosphate, which was previously bound to soil, into solution when added to soil alone

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Abbreviations: IHP, inositol hexaphosphate; KH_2PO_4, potassium phosphate; P_i, inorganic P; P_t, total P; P_o, organic P.

(Anderson et al., 1974). Additionally, as the concentration of added IHP increased, Fe and Al solution concentrations increased, whereas, the absolute amount of IHP sorbed increased then decreased. This was probably caused by the formation of soluble complexes of Al and Fe with IHP (Anderson et al., 1974). These studies suggest that organic P (P_o) in manures may compete for binding sites on soil surfaces and potentially reduce inorganic P (P_i) sorption.

The increase in sorption capacity with manure application observed in previously mentioned research is less well understood. Appelt et al. (1975) suggested increases in P sorption capacity may be caused by complexation of organic acids with Al and Fe from soil minerals giving rise to new P sorption sites on the complexes where hydroxyl groups are exchanged for phosphate. Whereas, others found that low molecular weight organic acids increase solubility of solid-phase Al in soils (Stumm, 1986; Fox et al., 1990). Organic acids influence the release of P and Al from surfaces in soils by formation of stable complexes with Al, which is dependent on the stability constant of the ligand (Fox et al., 1990). The dissolution of Al containing solids may give rise to new P sorption sites on the freshly scoured soil surfaces.

Some authors have reported a reduction in P sorption strength with the application of amendments but few have given explanations as to why this reduction in sorption strength likely occurs (Mozaffari and Sims, 1994; Sharpley, 1996; Holford et al., 1997; Siddique and Robinson, 2003; Laboski and Lamb, 2004). Barrow et al. (1998) suggested that reductions in P buffer capacity with addition of P fertilizers results as "phosphate ions slowly penetrate the reacting soil particle, producing a semi-permanent increase in negative charge and decrease in electric potential." Holford et al. (1997) suggested that the observed reduction in sorption strength with manure or effluent application history was likely caused by organic anion interaction with sorbing P anions, thus lowering the sorption strength. Both Holford et al. (1997) and Laboski and Lamb (2004) concluded that P sorption strength may have a greater impact on P availability than P sorption capacity and is possibly the more environmentally important sorption parameter because the reduction in P sorption strength with application of amendments resulted in a greater amount of P in soil solution at any given level of P sorbed.

The previously cited comparisons were made by constructing sorption isotherms before and after application of manure, either in an incubation study or in a field setting, using KH_2PO_4 as the source of P in the isotherm characterization. Limited research has been conducted on P sorption where manure is the source of P in the sorption solutions. Bhat and O'Callaghan (1980) found that more P_i sorbed to soil from solutions of pig slurry than KH_2PO_4. However, the sorption solutions were not treated to inhibit microbial activity. Thus, it is likely that some of the observed increase in P sorption was actually microbial consumption of P. Additionally, the solution matrix, unbuffered 0.01 M KCl, had a low ionic strength and the pH was not buffered. This matrix may have permitted the pig slurry to control ionic

strength and perhaps pH for some solutions over the range in P concentrations.

A standard P sorption procedure was published by Nair et al. (1984) to provide a reproducible method that would allow for comparison of isotherm coefficients from different research. This procedure uses a range of low P concentration solutions, prepared from KH_2PO_4, in unbuffered 0.01 M $CaCl_2$. Precipitation of Ca phosphates would likely occur, if this procedure is used when manure is the source of P because manure generally has high Ca concentrations. The addition of Ca ions in the manure sorption solution matrix would likely cause the solution to be supersaturated with respect to Ca phosphate compounds. An unbuffered system would likely result in solutions with pH greater than 7, further increasing the possibility of Ca phosphate precipitation if the pH is not fixed. In addition, the ionic strength of the sorption solution matrix suggested by Nair et al. (1984) is likely less than the ionic strength of diluted manure slurries. If sorption solutions with manure as the P source are prepared in unbuffered 0.01 M $CaCl_2$, the ionic strength of the sorption solutions would increase as the concentration of P in solution increases because the ionic strength is being controlled by the amount of slurry used. Controlling ionic strength throughout the entire P concentration range of the sorption solutions is important because an increase in ionic strength has been shown to enhance P sorption (Ryden and Syers, 1975).

The effects of ionic strength, cation species, and pH on P sorption have been studied previously. Ryden and Syers (1975) found that ionic strength and cation species both affected P sorption when four New Zealand soils were equilibrated for 40 h with P sorption solutions with varying cations and ionic strength. They suggest that if a rapid equilibration time is desired then a solution matrix of high ionic strength with a divalent cation should be used. To avoid precipitation of phosphate compounds when high P additions are used, Ryden and Syers (1975) suggest the use of a solution matrix of high ionic strength with cations of soluble phosphates such as sodium or potassium.

The objectives of this study were to: (i) develop a procedure to characterize how P_i and total P (P_t) from dairy slurry and swine slurry sorbs to soil; and (ii) compare the sorption characteristics of P_i and P_t when dairy slurry, swine slurry, and KH_2PO_4 are used as the P sources. The information obtained will aid in understanding the ability of soil to sorb P directly from manure and highlight potential implications for nutrient management.

MATERIALS AND METHODS

Soil and Manure

Six surface soils (0–0.15 m) used in these experiments were collected in southern, central Michigan and are described in Table 1. Soils selected had no history of manure application, Bray 1-P <30 mg P kg^{-1}, pH < 7, and varied in soil texture. These selection criteria were employed to reduce initial desorption of P and minimize Ca phosphate precipitation. Before experimentation, soils were air dried, sieved (2-mm sieve) and mixed thoroughly to ensure homogeneity. Soils were characterized by measuring pH, organic matter, cation exchange

Table 1. Soil classification and characterization.

Soil series	Classification	pH 1:1 H_2O	Organic matter	Sand	Silt	Clay	CEC†	Bray 1-P
			%				$cmol_c\ kg^{-1}$	$mg\ kg^{-1}$
Capac	fine-loamy, mixed, semiactive, mesic Aquic Glossudalf	6.4	2.9	32	37	31	11.7	14
Colwood 1	fine-loamy, mixed, active, mesic Typic Endoaquoll	5.6	5.4	42	36	22	16.4	15
Colwood 2	fine-loamy, mixed, active, mesic Typic Endoaquoll	5.3	6.1	48	40	12	16.9	8
Oshtemo	coarse loamy, mixed, active, mesic Typic Hapludalf	5.4	2.5	68	23	9	8.3	11
Parkhill	fine-loamy, mixed, semiactive, nonacid, mesic Mollic Endoaquepts	6.7	5.2	32	39	29	20.1	4
Spinks	sandy, mixed, mesic Lamellic Hapludalf	4.7	4.5	76	19	5	5.4	14

† Cation exchange capacity.

capacity, and Bray 1-P (Brown, 1998). Soil particle size was determined by the hydrometer method (Gee and Bauder, 1986).

The dairy slurry used in this experiment was collected from a short-term storage pit near a feeding facility. The pit was agitated before sample collection to ensure sample homogeneity. The swine slurry used in this experiment was collected from a slotted floor feeder house at the time of cleaning. Both dairy and swine manure were collected from animals fed traditional diets. Once collected, manures were individually mixed and sieved (2-mm sieve) to facilitate pipetting by removing large residual particles. Manures were characterized by measuring percent solids, total N, total P, soluble salts (K, Ca, Mg, and Na), Al, and Fe (Table 2) (Peters, 2003). After collection and sieving, manures were stored in polyethylene containers at 0°C. Aliquots of manure from each species were thawed and stored at 4°C as needed.

Sorption Procedure Determination

The standard P sorption procedure of Nair et al. (1984) used unbuffered KH_2PO_4 solutions in 0.01 M $CaCl_2$. The speciation model Phreeqc (Parkhurst, 1995) predicted that Ca phosphate compounds would precipitate at high P solution concentrations when manure composition was entered into the model with the background solution matrix proposed by Nair et al. (1984) (unbuffered 0.01 M $CaCl_2$). To prevent precipitation, the sorption solution pH was fixed at the average soil pH of 6 and 0.1 M KCl was used as the background electrolyte.

The electrolyte concentration was determined by comparing the conductivity of P solutions (0, 50, 75, and 100 mg P L^{-1}) with dairy slurry or swine slurry as the P source that were prepared in 0.05, 0.07, or 0.1 M KCl (data not shown). The necessary molarity of KCl was determined to be 0.1 M KCl because of the low variability of electrical conductivity between solutions prepared with 0 up to 100 mg total P L^{-1} when manure was the P source.

Other deviations from the Nair et al. (1984) method included the addition of chloroform and filtration method. Chloroform (in 0.75% ethanol; EM Science, guaranteed reagent; Gibbstown, NJ) was added at a rate of 0.16 mL of chloroform to 25 mL of solution. This ratio is about half that proposed by Nair et al. (1984), but was experimentally determined, by plating samples with and without chloroform and counting

colony forming units for a period of 4 d, to be adequate in suppressing microbial activity for the 24-h equilibration period. Nair et al. (1984) proposed the use of 0.45-μm filter paper for filtration of equilibrated solutions. However, this form of filtration is very time consuming and costly. Thus, filtration with 0.45-μm filtration disc units (Millex Millipore Corp., Bedford, MA) and Whatman no. 1 filter paper (Whatman International Ltd, Maidstone, England) along with no filtration were tested using manure slurries and KH_2PO_4 solutions to determine if there were differences in P_i solution concentrations for these filtration methods after samples were centrifuged at 2350 × g for 10 min. After samples were centrifuged, for each P source, concentrations of P_i in solution were not different between filtration with Whatman no. 1 filter paper, 0.45-μm filter disc units, or no filtration (data not shown). Whatman no. 1 filter paper in conjunction with centrifugation was chosen because it could remove large floating particles, was inexpensive, and provided data comparable to filtration with 0.45-μm filter disc units. Baxter et al. (2003) also used a combination of centrifugation and filtration with a more porous paper in lieu of 0.45-μm filtration.

Comparison of Isotherms Produced with Different Solution Matrices

To determine if variations in cation and ionic strength of the sorption solutions created sorption isotherms with different sorption characteristics, two separate sorption experiments were conducted. In the first experiment, P solutions (ranging in concentration from 0 to 50 mg P L^{-1}) were prepared from KH_2PO_4 in unbuffered 0.01 M $CaCl_2$. In the second experiment, P solutions (ranging in concentration from 0 to 50 mg P L^{-1}) were prepared from KH_2PO_4 in 0.1 M KCl, pH 6. In both experiments, soils were equilibrated, for 24 h in an end-over-end shaker, with the P solutions at a 1:25 (w/v) soil/solution ratio with the addition of 0.16 mL of chloroform to 25 mL of solution to inhibit microbial activity. After equilibration, samples were centrifuged for 10 min at 2350 × g and filtered through Whatman no. 1 filter paper. The amount of P sorbed was determined by the difference in the concentration of P initially added and the concentration of P in solution at the end of the equilibration period. Sorption isotherms were measured in triplicate.

Table 2. Characterization of dairy and swine manure slurries.

Species	Solids	N	P_t†	P_i†	K	Ca	Mg	Na	Al	Fe
	%					$mg\ L^{-1}$				
Dairy	4.7	3271	530	420	2228	1618	539	647	21	57
Swine	5.2	6542	1254	1102	3810	1078	648	755	53	151

† P_t, total P; P_i, inorganic P.

Determination of Phosphorus Sorption from Different Phosphorus Sources

Phosphorus sorption experiments were conducted using three different sources of P: KH_2PO_4, dairy slurry, and swine slurry. Sorption solutions were prepared on an approximate P_t basis, using the nutrient characteristics of whole sieved manures, to contain a range of P concentrations between 0 and 75 mg P_t L^{-1} (Table 3). Actual solution P_t concentrations ranged from 0 to 75 mg P L^{-1} for KH_2PO_4, 0 to 70 mg P_t L^{-1} for dairy slurry, and 0 to 63 mg P_t L^{-1} for swine slurry (Table 3). Solutions were prepared in 0.1 M KCl at pH 6. Phosphorus sorption solutions were added to soil at a 1:25 (w/v) soil/ solution ratio. Chloroform was added to inhibit microbial activity at a rate of 0.16 mL of chloroform to 25 mL of solution. Solutions were equilibrated for 24 h in an end-over-end shaker, and then centrifuged at 2350 × g for 10 min. A portion of the centrifuged sample was filtered through Whatman no. 1 filter paper and analyzed for P_i. The remaining supernatant of the centrifuged sample was stored at 4°C until digestion and analysis for P_t and analysis for Al and Fe. Sorption isotherms were measured in quadruplicate.

Differences in sorption solution P_i concentrations caused by P transformations were noticed when initial P_i values were determined daily from solutions stored at 4°C. Therefore, for each replication, initial P_i values for each manure solution were determined in duplicate by placing 25 mL of each sorption solution and 0.16 mL of chloroform in a 50-mL centrifuge tube and shaking for 24 h under the same conditions as the samples.

Phosphorus Analysis

All samples were analyzed for P_i by the ascorbic acid colorimetric method at a wavelength of 882 nm (Frank et al., 1998). The amount of P_i sorbed was determined by the difference between the concentration of P_i initially added and the concentration of P_i in solution at the end of the equilibration period.

For P_t analysis, samples were digested according to the persulfate oxidation method of Bender and Wood (2000) with some modifications. Aliquots of equilibrated samples (5 or 10 mL) were diluted to a final volume of 50 mL with distilled water. Diluted samples were then digested with 0.7 g potassium persulfate and 1 mL of 5.5 M H_2SO_4. The optimum amount of potassium persulfate needed for complete digestion was greater than that proposed by Bender and Wood (2000) and was determined in a separate experiment (data not provided). Samples were first digested for 1.25 h at approximately 100°C, and then the hotplate was turned to the maximum setting to increase boiling, until the samples were reduced to approximately 10 mL. Cooled samples were diluted with 30 mL of distilled water. After samples were diluted, approximately 5 mL of 2 M NaOH was added to adjust the pH of the solution. Solutions were transferred to volumetric flasks and diluted to a final volume of 100 mL. Phosphorus in diluted digested samples was analyzed by the ascorbic acid colorimetric method at a wavelength of 882 nm (Frank et al., 1998). Digested standards of KH_2PO_4 were used to produce the standard curve for determination of the concentration of P_t in solution. The amount of P_t sorbed was determined by the difference between the concentration of P_t initially added and the concentration of P_t in solution at the end of the equilibration period.

The amount of P_o remaining in solution after equilibration was determined by the difference between the amount of P_t in solution and the amount of P_i in solution. Likewise, the amount of P_o sorbed was determined by the difference between the amount of P_t and P_i sorbed.

Aluminum and Iron Solution Concentrations

Samples were analyzed for Al and Fe concentrations in solution to determine if manure slurry solutions caused dissolution of Al and Fe from soil colloid surfaces. All samples (both initial and final solutions) were spiked after centrifugation with 5 mg L^{-1} each of Al and Fe to ensure values above the 1 mg L^{-1} method detection limit. Spiked samples were analyzed for Al and Fe in solution using a direct current plasma spectrometer (DCP) (SpectraSpan V, Andover, MA). The amount of Al and Fe desorbed was calculated by the difference between the amount of Al and Fe in solution initially and the amount in solution after equilibration.

Data Analysis

Phosphorus Sorption Isotherms

Nonlinear regression was used to fit P_i and P_t sorption data to the Langmuir equation which is given by:

$$Q = \frac{bkC}{1 + kC} \quad [1]$$

where Q is the amount of P sorbed to the soil (mg P kg^{-1}), C is the amount of P in the solution after equilibration (mg P L^{-1}), b is the sorption maxima (mg P kg^{-1}), and k is the sorption strength (L mg^{-1}). Nonlinear regression was used to obtain estimates and standard errors of the b and k parameters (NLIN procedure; SAS Institute, 1999). Comparisons of b and k terms between two data sets were made using nonlinear regression in a procedure similar to comparing regression coefficients in linear regression (Cook and Weisberg, 1999; Freud and Littell, 2000; Laboski and Lamb, 2004). The P_o sorption isotherms did not fit the Langmuir equation.

Table 3. Characterization of inorganic P (P_i) and total P (P_t) in the sorption solutions.

Sorption solution	Dairy			Swine			KH_2PO_4
	P_i†	P_t‡	P_i as percentage of P_t	P_i†	P_t‡	P_i as percentage of P_t	P
	mg L^{-1}		%	mg L^{-1}		%	mg L^{-1}
1	0	0		0	0		0
2	1.3	1.6	81	1.9	2.0	95	2
3	3.4	4.0	85	4.5	4.7	96	5
4	6.8	7.9	86	8.8	9.1	97	10
5	10.0	11.8	85	13.4	14.0	96	15
6	13.3	15.3	87	17.3	18.0	96	20
7	20.5	23.0	89	25.1	26.5	95	30
8	33.0	37.8	87	41.9	42.9	98	50
9	49.3	57.3	86	60.3	63.1	96	75
10	69.8	70.1	100	–	–	–	–

† Average (eight replications) initial inorganic P (P_i) solution concentration of centrifuged samples.
‡ Average (eight replications) initial total P (P_t) solution concentration, of centrifuged samples.

Relationship between Phosphorus and Aluminum and Iron

To investigate whether differences in either P_i or P_t sorption capacities between the manure sources were related to desorption of Al or Fe from soil surfaces, the following analysis was employed. First, because discrete data points for the three P sources at precisely the same solution P concentrations did not exist, Q values for KH_2PO_4 were computed by substituting the experimentally determined C values of a given slurry into the Langmuir equation for sorption from KH_2PO_4 for each data point from the manure slurries. These calculated KH_2PO_4–Q values were then subtracted from the experimentally derived Q values for the respective slurry to obtain the difference in P_i or P_t sorbed between the slurries and KH_2PO_4. Next, the Al and Fe desorbed during the equilibration of each slurry-soil sample were correlated with the differences in P_i or P_t sorption calculated in the first step.

RESULTS AND DISCUSSION

Comparison of Sorption Solution Matrices

Phosphorus sorption capacity (b) for the two P sorption solution matrices were not significantly ($\alpha = 0.05$) different for all soils (Table 4). Phosphorus sorption strength (k) for the two solution matrices was not significantly different for all soils except Oshtemo and Colwood 2. Overall, these two solution matrices yielded sorption isotherms that were not considerably different. Most importantly, a sorption matrix was developed such that precipitation and ionic strength interferences were minimized. Hence, a matrix of 0.1 M KCl at pH 6 was used to prepare manure sorption solutions and will provide results comparable to research using an unbuffered 0.01 M CaCl$_2$ solution matrix.

Aluminum and Iron Solution Concentrations

For all soils, Al and Fe desorbed from soil constituents for both slurries and KH_2PO_4 (Table 5). Aluminum and Fe desorption in soils equilibrated with dairy slurry was an order of magnitude greater than Al and Fe desorption in swine slurry or KH_2PO_4. Traina et al. (1986),

Table 4. Comparison of Langmuir parameters for standard (CaCl$_2$) and developed (KCl) P sorption matrices for the six soils.

Soil series	Sorption solution matrix	Langmuir parameters†		
		b	k	R^2
		mg kg^{-1}	L mg^{-1}	
Capac	CaCl$_2$‡	265a¶	0.270a	0.97
	KCl§	261a	0.201a	0.96
Colwood 1	CaCl$_2$	476a	0.217a	0.98
	KCl	481a	0.175a	0.98
Colwood 2	CaCl$_2$	175a	0.070a	0.97
	KCl	207a	0.038b	0.99
Oshtemo	CaCl$_2$	106a	0.231a	0.96
	KCl	109a	0.141b	0.97
Parkhill	CaCl$_2$	329a	0.200a	0.96
	CaCl$_2$	294a	0.180a	0.96
Spinks	KCl	369a	0.311a	0.97
	CaCl$_2$	363a	0.301a	0.97

† b, sorption capacity (mg kg^{-1}); k, sorption strength (L mg^{-1}).
‡ CaCl$_2$, standard matrix using unbuffered 0.01 M CaCl$_2$.
§ KCl, developed matrix using 0.1 M KCl at pH 6.0.
¶ Within a soil series, values within each column followed by the same letter are not significantly different ($\alpha = 0.05$).

Table 5. Concentration of Al and Fe sorbed for each soil and P source during the P sorption experiment.

P Source	Soil	Al sorbed†	Fe sorbed†
		mg L^{-1}	
Dairy	Capac	−1.72	−1.16
	Colwood 1	−3.26	−1.41
	Colwood 2	−4.78	−2.29
	Oshtemo	−2.16	−0.67
	Parkhill	−7.78	−3.63
	Spinks	−3.57	−2.79
Swine	Capac	−1.57	−0.87
	Colwood 1	−0.25	0.01
	Colwood 2	−0.01	0.08
	Oshtemo	−0.43	−0.24
	Parkhill	0.15	0.23
	Spinks	−0.40	−0.36
KH_2PO_4	Capac	−0.28	−0.20
	Colwood 1	−0.47	−0.25
	Colwood 2	−0.40	−0.22
	Oshtemo	−0.01	−0.01
	Parkhill	−0.21	−0.33
	Spinks	−0.46	−0.29

† Data are the mean of the replications for the solution of highest P concentration for each P source. Aluminum or Fe sorbed is calculated as the amount of Al or Fe in the final solution subtracted from the amount initially added. Negative sorption values mean desorption occurred.

Fox et al. (1990), and Ohno and Crannell (1996) have shown that concentration and type of organic acid impact the solubility of solid phase Al in soil. Additionally, Anderson et al. (1974) found that Al and Fe release was related to the addition of an organic P compound. Thus, differences in dissolution of Al and Fe for the two manure sources may be caused by differences in the concentrations and type of organic acids or P_o compounds in the different manure species. Organic acid type and concentration were not measured for the manures used in this study. However, differences in organic acid compositions and concentration, dissolved organic C, and P_o compounds between the manures could likely occur and be caused by differences in animal diet, physiology, and perhaps manure storage.

Phosphorus Sorption Capacity

For all soils, P_i sorption capacity (b) was significantly ($\alpha = 0.05$) greater for dairy slurry than swine slurry or KH_2PO_4 (Table 6). Inorganic P sorption capacity for swine slurry was significantly less than that of KH_2PO_4 for Capac, Colwood 1, Parkhill, and Spinks soils, but was not significantly different than KH_2PO_4 for Colwood 2 and Oshtemo soils.

For all soils, P_t sorption capacity was significantly greater for both dairy and swine slurries compared to KH_2PO_4 (Table 6). For Capac, Colwood 1, and Spinks soils, P_t sorption capacity was significantly greater for dairy slurry than swine slurry, but dairy slurry was not significantly different than swine slurry for all other soils. For Capac, Colwood 2, Oshtemo, and Parkhill soils, P_t sorption capacity was significantly ($\alpha = 0.05$) greater than P_i sorption capacity for dairy slurry. While for the Colwood 1 and Spinks soils, P_i and P_t sorption capacities for dairy slurry were not significantly different. Total P sorption capacity of swine slurry was significantly greater than P_i sorption capacity of swine slurry for all soils.

The small amount of Al and Fe released with the addition of swine slurry was not correlated to the reduction in

Table 6. Effect of P source on Langmuir parameters for selected soils.

| Soil series | Source | Langmuir parameters† | | |
		b	k	R^2
		mg kg^{-1}	L mg^{-1}	
Capac	P_i KH$_2$PO$_4$	261a‡	0.201a	0.96
	P_i Dairy	329b	0.135b	0.95
	P_t Dairy	439c	0.087c	0.94
	P_i Swine	172d	0.180abc	0.97
	P_t Swine	297e	0.238a	0.95
Colwood 1	P_i KH$_2$PO$_4$	481a	0.175a	0.98
	P_i Dairy	713b	0.107b	0.97
	P_t Dairy	741b	0.089b	0.98
	P_i Swine	318c	0.175a	0.98
	P_t Swine	604d	0.161a	0.97
Colwood 2	P_i KH$_2$PO$_4$	207a	0.038a	0.99
	P_i Dairy	362b	0.105a	0.98
	P_t Dairy	577c	0.016b	0.98
	P_i Swine	212a	0.027ab	0.99
	P_t Swine	676c	0.012b	0.96
Oshtemo	P_i KH$_2$PO$_4$	109a	0.141a	0.97
	P_i Dairy	144b	0.123a	0.95
	P_t Dairy	181c	0.091b	0.98
	P_i Swine	114a	0.063c	0.96
	P_t Swine	181c	0.091abc	0.91
Parkhill	P_i KH$_2$PO$_4$	294a	0.180a	0.96
	P_i Dairy	374b	0.098b	0.96
	P_t Dairy	437c	0.081b	0.95
	P_i Swine	191d	0.146ab	0.97
	P_t Swine	394bc	0.115b	0.93
Spinks	P_i KH$_2$PO$_4$	363a	0.301a	0.97
	P_i Dairy	671b	0.109b	0.96
	P_t Dairy	692b	0.081b	0.97
	P_i Swine	272c	0.225ac	0.98
	P_t Swine	517d	0.179c	0.97

† b, sorption capacity (mg kg^{-1}); k, sorption strength (L mg^{-1}).
‡ For a given soil, values within a column followed by the same letter are not significantly different at $\alpha = 0.05$.

P_i sorption capacity of the swine slurry compared to KH$_2$PO$_4$ (Table 7). Because of this, if a correlation exists for Al or Fe desorbed and the difference between P_t sorption for swine slurry and KH$_2$PO$_4$ (Table 8), then the relationship would be related to the formation of P_o and Al or Fe complexes. In general, there was no significant correlation of desorbed Al or Fe to the increase in P_t sorption capacity with the addition of swine slurry, meaning that P_o complexes with Al and Fe were not forming or played a minor role in P sorption from swine slurry.

Organic P sorption can be roughly calculated as the difference between sorption capacity for P_t and P_i. For any given soil, P_o sorption is greater for swine slurry compared to dairy slurry (Table 6). Additionally, P_o sorption

Table 7. Correlation (r) of desorbed Fe or Al and the difference between inorganic P sorption capacity from each slurry and KH$_2$PO$_4$.

| P source | Soil | Fe | | Al | |
		r	P value	r	P value
Dairy	Capac	−0.29	0.0937	−0.44	0.0078
	Colwood 1	−0.28	0.1042	−0.48	0.0041
	Colwood 2	−0.58	0.0002	−0.70	<0.0001
	Oshtemo	−0.42	0.0117	−0.57	0.0003
	Parkhill	−0.46	0.0009	−0.46	0.0086
	Spinks	−0.64	<0.0001	−0.72	<0.0001
Swine	Capac	0.27	0.1502	0.43	0.0206
	Colwood 1	0.03	0.8673	0.27	0.1291
	Colwood 2	0.35	0.0637	0.20	0.2880
	Oshtemo	0.06	0.7380	0.13	0.4825
	Parkhill	0.001	0.9954	0.04	0.8331
	Spinks	0.25	0.1795	0.15	0.4180

Table 8. Correlation (r) of desorbed Fe or Al and the difference between total P sorption capacity from each slurry and KH$_2$PO$_4$.

| P source | Soil | Fe | | Al | |
		r	P value	r	P value
Dairy	Capac	0.32	0.0761	0.36	0.0427
	Colwood 1	−0.05	0.7875	0.01	0.9443
	Colwood 2	−0.04	0.8457	−0.01	0.9616
	Oshtemo	0.18	0.3162	0.22	0.2234
	Parkhill	−0.17	0.3572	−0.13	0.4704
	Spinks	−0.27	0.1122	−0.19	0.2768
Swine	Capac	−0.26	0.1764	−0.29	0.1221
	Colwood 1	−0.05	0.7700	−0.03	0.8611
	Colwood 2	−0.49	0.0207	−0.31	0.1627
	Oshtemo	−0.03	0.8850	−0.002	0.9927
	Parkhill	0.16	0.4159	0.07	0.7250
	Spinks	−0.10	0.6094	−0.05	0.7920

capacity of the soils is 37 to 69% of P_t sorption capacity for swine slurry and 4 to 37% of P_t sorption capacity for dairy slurry (calculated from data in Table 6). On average, P_o was 13% of P_t in the dairy solutions and 4% in the swine solutions (Table 3). Therefore, these soils have a greater selectivity for P_o compared to P_i from swine slurry because P_o made up 4% of P_t in the solution and accounted for 37 to 69% of P_t sorption. Preferential sorption of P_o from dairy slurry was not apparent. These data suggest that the preferential sorption of P_o from swine slurry caused the reduction in P_i sorption. Data from Anderson et al. (1974) support this theory in that they found preferential sorption of P_o and reduced P_i sorption as P_o concentrations in solution increased.

One hypothesis for the increase in P sorption capacity observed by dairy slurry compared to KH$_2$PO$_4$ is that new sorption sites were created by the dissolution of Al and Fe from soil surfaces by low molecular weight organic acids. Differences between P_i sorbed from dairy slurry and KH$_2$PO$_4$ were moderately to strongly correlated to desorbed Al ($r = -0.44$ to -0.72) for all soils (Table 7), while differences between P_i sorbed from dairy slurry and KH$_2$PO$_4$ were moderately correlated to desorbed Fe ($r = -0.42$ to -0.64) for all soils except Capac and Colwood 1. Differences between P_t sorbed from dairy slurry and KH$_2$PO$_4$ were not correlated to desorbed Al or Fe (Table 8).

These results support the theory of creation of new P sorption sites caused by the dissolution of Al and Fe from soil surfaces by dairy slurry; likely allowing newly exposed Al and Fe on soil surfaces to sorb P. In addition, desorbed Al and Fe may be forming complexes with the added dissolved organic C from the dairy slurry possibly forming new P-binding sites. It is also possible that P is binding to desorbed Al and Fe and is being considered sorbed to soil. These results are contrary to the results of Ohno and Crannell (1996), where P_i sorption was decreased by the addition of dissolved organic C from green manures, which increased dissolution of Al and Fe. The differences in the relationship between P sorption and Al and Fe dissolution between this research and that of Ohno and Crannell (1996) is likely related to the differences in the composition of dissolved organic C, including short chain organic acids and humic and fulvic acids, the presence of P_o in this study and lack of P_o in their study, and the pH of the sorption solutions.

Phosphorus Sorption Strength

Inorganic P sorption strength (k) of the dairy slurry was significantly ($\alpha = 0.05$) less than KH_2PO_4 for Capac, Colwood 1, Parkhill, and Spinks soils, but not for the other soils (Table 6). Inorganic P sorption strength of swine slurry was significantly less than KH_2PO_4 only for the Oshtemo soil. Inorganic P sorption strength of dairy slurry was not significantly different than swine slurry for Capac, Colwood 2, and Parkhill soils, was significantly less than swine slurry for Colwood 1 and Spinks soils, and was significantly greater than swine slurry for Oshtemo soil.

For all soils, P_t sorption strength of dairy slurry was significantly less than the sorption strength of KH_2PO_4. Total P sorption strength of the swine slurry was significantly less than sorption strength of KH_2PO_4 for Colwood 2, Parkhill, and Spinks soils, but not for Capac, Colwood 1, and Oshtemo soils. For Capac, Colwood 1, and Spinks soils, P_t sorption strength was significantly less for dairy slurry compared to swine slurry, but was not significantly different than swine slurry for all other soils.

For all soils, P_i sorption strength was not significantly different than P_t sorption strength of swine slurry. Inorganic P sorption strength was significantly greater than P_t sorption strength of dairy slurry only for Capac, Colwood 1, Colwood 2, and Oshtemo soils.

Overall, P_i sorption strength of the manure slurries was less than KH_2PO_4. However, this trend was not always significant. Total P sorption strength of dairy slurry was significantly less than KH_2PO_4 for all soils. Total P sorption strength for swine slurry was generally less than KH_2PO_4, but this difference was not always significant. Holford et al. (1974) describes sorption strength, as modeled by the Langmuir equation, as the average of low and high strength sorption sites. Thus, the observed reduction in P_t sorption strength may be caused by the P_o portion of the manure slurries binding to soils, likely at lower sorption strength sites. This may occur because P_t is the sum of P_i and P_o and for the mean sorption strength of P_t to be less than P_i, the sorption strength of P_o would have to be less than P_i. Reduced P_i and P_t sorption strength observed in this experiment for dairy slurry is hypothesized to be caused by: (i) the low sorption strength associated with the newly created sites on the soil surface by the dissolution of Al and Fe by organic acids; or (ii) the low binding strength of the newly created sites on enlarged organic matter-Fe surface complexes as suggested by Holford et al. (1997). Reduced P_i sorption strength observed for swine slurry compared to KH_2PO_4 is hypothesized to be caused by the competition of P_o for P sorption sites that possibly bind to the high strength sites leaving the lower sorption strength sites for P_i binding.

Correlation of Sorption Properties with Soil Characteristics

Correlation between soil properties and the b and k terms of the Langmuir equation for each soil-P source combination along with the difference in P_i and P_t sorption between manure slurries and KH_2PO_4 were deter- mined. For the most part, correlations obtained between sorption properties and soil characteristics were not significant. However, organic matter was significantly correlated to P_t sorption capacity of swine slurry ($P = 0.0111$) and P_i sorption strength of dairy slurry ($P = 0.0294$), while silt content was correlated to the difference in P_t sorption capacity between swine slurry and KH_2PO_4 ($P = 0.0669$). Overall, soil characteristics could not account for the fact that P sorption for a given P source did not behave the same way for all soils. Multiple regression of sorption parameters with soil characteristics was not explored as the sample population was small (six soils).

CONCLUSIONS

When KH_2PO_4 is used as the P source, the P sorption procedure outlined in this article provides data comparable to that obtained using the standard procedure of Nair et al. (1984). More importantly, this procedure can be used to obtain data on the sorption of P from manure slurries.

Dairy slurry and swine slurry, when used as the P source in sorption solutions, impacted P_i sorption capacity differently as compared to KH_2PO_4. The P_i sorption capacities for dairy slurry were greater and for swine slurry were less than for KH_2PO_4. Dairy slurry and swine slurry, when used as the P source, had a similar impact on P_t sorption capacity as compared to when KH_2PO_4 was the P source. Inorganic P and P_t sorption strength was generally reduced for both dairy and swine slurries as compared to KH_2PO_4. Desorption of Al and Fe was correlated to the difference in P_i sorption between dairy slurry and KH_2PO_4, but not between swine slurry and KH_2PO_4. For dairy slurry, P_i sorption is likely increased because P_i is binding to newly exposed Al and Fe on soil surfaces. Reduction in P_i sorption and increased P_t sorption from swine slurry is caused by the preferential sorption of P_o. The different mechanisms and relative importance of P_i and P_o sorption for the different slurries are likely related to composition and concentration of dissolved organic C and P_o compounds along with concentration and composition of short chain organic, humic, and fulvic acids.

The greater sorption capacity for dairy slurry suggests that it may increase soil test P less than fertilizer, while the reduction in sorption capacity by swine slurry suggests that it may increase soil test P more than fertilizer. These data may explain why Laboski and Lamb (2003) found that swine slurry increased soil test P more than KH_2PO_4 when incubated with soil at the same rate of total P. Additional studies need to be conducted to determine how differences in P sorption between manures and fertilizer impact in-field P availability to a crop. The results also suggest that dairy and swine slurry have an increased risk for P losses to surface water and leaching potential compared to inorganic fertilizers because of lower sorption strength. Future studies should seek to link P concentrations in surface water runoff with differential P sorption from manure and fertilizer using the same manures and fertilizers as field experiments.

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